Final Report: Linking Metal Ions via Inorganic Click (iClick) Reactions.

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Dates Covered: 08/15/2013 – 08/15/2015

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Grant #: DE-SC0010510

DOE/Office of Science Program Office: Basic Energy Sciences

DOE/Office of Science Program Manager Contact: Dr. Michael Sennett

Research area or areas (as identified in Part I): (a) Materials Chemistry

1.1. Final Report: LINKING METAL IONS VIA INORGANIC CLICK (ICLICK) REACTIONS

DE-SC0010510 OBJECTIVES (✓ completed; ✗, failed)

This one-year seed project (with one year no-cost extension) contained three objectives:

A) Expand the scope of iClick synthesis beyond Au^{I}/Au^{I} reactions. ✓

B) Elucidate a Cu^{I}-catalyzed iClick reaction. ✓/ ✗

C) Synthesize and characterize tri- and tetra-metallic complexes as models for metallopolymers. ✓

1.2. Brief Discussion of Completed Objectives

1.2.1. *A) Expand the scope of iClick synthesis beyond Au^{I}/Au^{I} reactions*. ✓ In 2011,[1] we reported the first iClick reaction between PPh_3AuN_3 (**1**) and $PPh_3AuC{\equiv}CPh$ (**2**) to provide the cycloaddition product $[PPh_3Au]_2(1,5\text{-}\mu\text{-}N_3C_2Ph)$ (**3**) (Figure 1). The reaction was the first example of linking metal ions between a triazolate bridge through a cycloaddition reaction. The term "inorganic click" or "iClick" reflects the participation of the metal ions in the cycloaddition, relative to the broadly applied[2] all organic alkyne/azide cycloaddition. One of the objectives of the seed project was to expand iClick beyond gold. The proposed work involved selecting different M-azide/M-acetylide partners to determine which combinations result in a cycloaddition. This objective was achieved and we were able to execute iClick reactions between Au(I), Rh(I), Ir(I), and Pt(II).[3,4]

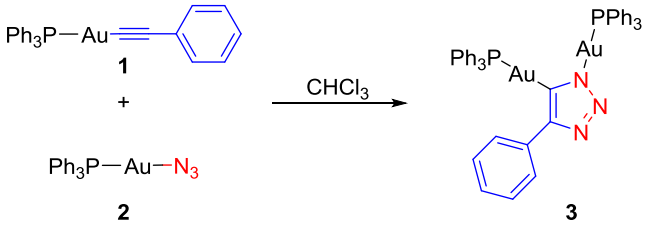

Figure 1. First iClick synthesis of the digold triazolate complex **3**.

1.2.2. *Lessons Learned.* During the seed project, a limitation of iClick was discovered: Au-acetylide is a prerequisite partner in the all-metal cycloaddition. We were unable to find any combination of M-acetylide/M-azides where the M-acetylide was not a member of group 11 that would undergo the cycloaddition. Curious as to the reason for this unforeseen limitation, we executed a kinetic/mechanistic study of the iClick reaction. The results we obtained clearly indicate the Au-acetylide partner in iClick is playing the role of the Cu-acetylide intermediate in traditional copper-catalyzed azide-alkyne cycloaddition (CuAAC).[5,6] The currently accepted mechanism and the results of our investigation are presented in Figure 2. This work is important to the community as well. The mechanistic data, though solid for copper, suffered from an inability to control the copper species to garner clean kinetic data. Since we are able to control the stoichiometry of both click partners our work provides the clearest kinetic data to support the metal-catalyzed azide-alkyne cycloaddition. The seed grant DE-SC0010510 was critical in giving us the opportunity to elucidate the fundamental principles of iClick and we are now able move forward to more focused materials applications.

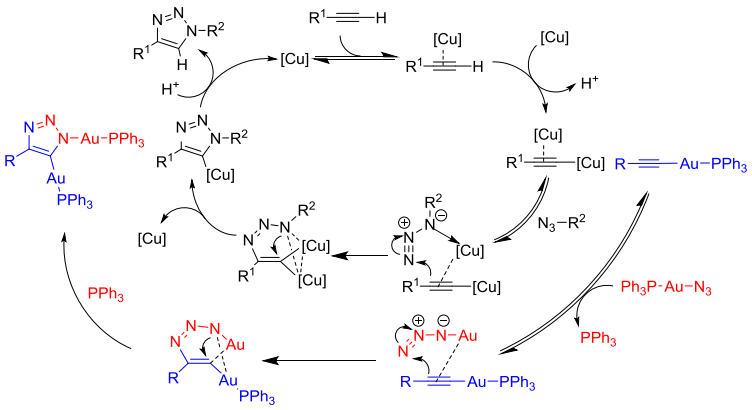

Figure 2. CuAAC mechanism overlaid with the proposed iClick mechanism.

1.2.3. *B) Elucidate a Cu^{I}-catalyzed iClick reaction.* ✔/✘ Motivated by a need to expand iClick beyond Au ions, the idea for this project was to elucidate a general method for coupling any two metal ion pairs via copper-catalyzed cycloaddition of a *terminal* M-acetylide and a M-azide. Copper ions activate the terminal C-H bond and therefore the choice of metal ion partners should not matter Figure 3. We were unable to find a general catalytic method in the project timeframe for this objective. Various copper sources were screened against several different M-acetylide/M-azide partners. Unfortunately, one of the pervasive side-reactions was Cu^{I} substitution at both the M-acetylide and M-azide sites. As a consequence, this aspect of the seed grant DE-SC0010510 will not be explored further. However, we did discover a set of conditions for catalyzing the cycloaddition between a M-acetylide and an "organic azide". This important result will permit future researchers to explore the synthesis of none-group 11 metallopolymers synthesis. Thus, the seed project again was critical in focusing future materials syntheses endeavors.

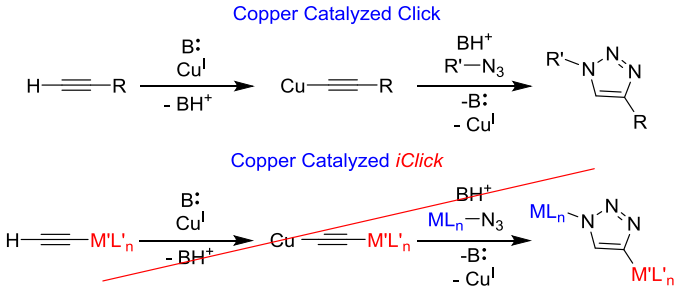

Figure 3. Cu(I) catalyzed Click and the proposed iClick version.

1.2.4. C) *Synthesize and characterize tri- and tetra-metallic complexes as models for metallopolymers.* ✔We are pleased to report that this objective was achieved during the seed project timeframe. For the first time,[7] we synthesized and characterized solution stable gold oligomers **6** and **8** that assemble via aurophilic interactions and iClick (Figure 4). By reducing the size of the PR_3 ligands and upon completing the iClick reaction between diacetylide complexes **5**/**7** and Et_3P-Au-N_3 (**4**) the new tetragold complexes **6**/**8** self-assemble in solution to give stable oligomers. Typically, aurophilic interactions are not strong enough to be stable in solution, and most are only observed in the solid state. Our complexes are stable in solution, and therefore are solution processable for optical materials. These discoveries open up many new opportunities to manipulate iClick for the purpose of light emitting materials; a prospect that was unknown at the initiation of the SEED grant.

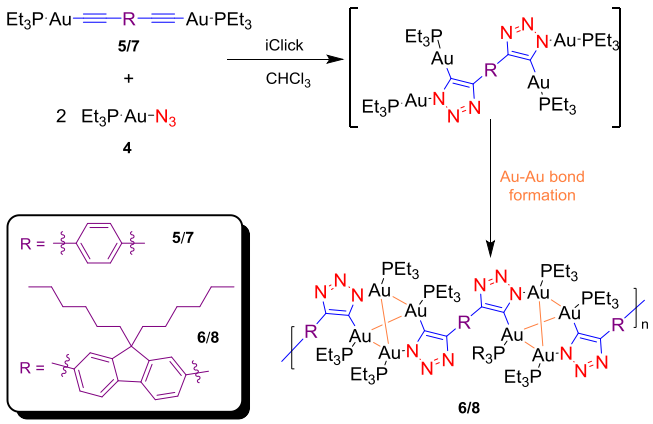

Figure 4. Construction of organogold oligomers via iClick and aurophilic interactions.

1.3. List of Publications from the One-year Seed Grant DE-SC0010510.

1. Beto, C. C.; Yang, X.; Powers, A. R.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S.* Expanding iClick to group 9 metals. *Polyhedron*, **2015**, *accepted* http://dx.doi.org/10.1016/j.poly.2015.08.032.
2. Powers, A. R.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S.* Au-iClick mirrors the mechanism of copper catalyzed azide-alkyne cycloaddition (CuAAC). *Dalton Trans.* **2015**, *44*, 14747-14752.
3. Yang, X.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *Organogold oligomers: exploiting iClick and aurophilic cluster formation to prepare solution stable Au_4 repeating units. Dalton Tran.* **2015**, *44*, 11437-11443.
4. Yang, X.; Trevor J. del Castillo, Ghiviriga, I.; Schanze, K. S.; Veige, A. S. *Copper-catalyzed cycloaddition between platinum-acetylides and organic azides.* **2015**, *in preparation*.

1.4. References Cited

(1) Del Castillo, T. J.; Sarkar, S.; Abboud, K. A.; Veige, A. S. *1,3-Dipolar cycloaddition between a metal-azide Ph_3PAuN_3 and a metal-acetylide $Ph_3PAuCCPh$: an inorganic version of a click reaction. Dalton Trans.* **2011**, *40*, 8140-8144. http://dx.doi.org/10.1039/c1dt10787a

(2) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Click chemistry: Diverse chemical function from a few good reactions. Angew. Chem. Int. Ed.* **2001**, *40*, 2004-2021. http://dx.doi.org/10.1002/1521-3773(20010601)

(3) Beto, C. C.; Yang, X.; Powers, A. R.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *Exapanding iClick to group 9 metals. Polyhedron* **2015**, *aceppted*. http://dx.doi.org/10.1016/j.poly.2015.08.032

(4) Powers, A. R.; Yang, X.; Del Castillo, T. J.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *Inorganic click (iClick) synthesis of heterotrinuclear Pt^{II}/Au_2^{I} complexes. Dalton Trans.* **2013**, *42*, 14963-14966. http://dx.doi.org/10.1039/C3dt52105b

(5) Tornøe, C. W.; Christensen, C.; Meldal, M. *Peptidotriazoles on solid phase: [1,2,3]-triazoles by regiospecific copper(I)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides. J. Org. Chem.* **2002**, *67*, 3057-3064. http://dx.doi.org/10.1021/Jo011148j

(6) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *A stepwise Huisgen cycloaddition process: Copper(I)-catalyzed regioselective "ligation" of azides and terminal alkynes. Angew. Chem. Int. Ed.* **2002**, *41*, 2596-2599. http://dx.doi.org/10.1002/1521-3773(20020715)41:14<2596::AID-ANIE2596>3.0.CO;2-4

(7) Yang, X.; Wang, S.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *Organogold oligomers: exploiting iClick and aurophilic cluster formation to prepare solution stable Au_4 repeating units. Dalton Trans.* **2015**, *44*, 11437-11443. http://dx.doi.org/10.1039/c5dt00282f